NUCLEAR MAGNETIC RESONANCE AND ACTIVATION ENERGY OF SEGMENTAL MOTION IN POLYMERS*

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THE motion of macromolecules and their components (various "pendants", segments, etc.) is usually described by the correlation time τ, the temperature dependence of which is exponential in nature

$$\tau=\tau_0 \exp (E/RT), \tag{1}$$

where τ_0 is the pre-exponential factor, E—the activation energy of the type of motion, R—gas constant, T—temperature.

It is normally assumed that τ_0 and E are independent of T and the value of τ can be determined from measurements of dielectric and mechanical losses, viscosity, etc.

By studying segmental motion in polymers by nuclear magnetic resonance (NMR) it is possible to determine correlation times (denoted as τ_c) firstly from the temperature dependence of the width δ of the absorption line (or spin-spin relaxation time T_2 making a certain assumption regarding the shape of the line) in the range of a marked variation according to formula (1)

$$\tau_c=\frac{1}{\alpha\gamma\delta}\tan\frac{\pi}{2}\frac{\delta^2-\delta_d^2}{\delta_T^2-\delta_d^2}, \tag{2}$$

where α is the gyromagnetic ratio of the resonant nucleus; γ, a constant of the order of unity [1], or $\sim 0{\cdot}16$ [2]; δ_d and δ_T line width with and without well-developed motion, respectively.

Secondly, from the temperature dependence of the spin-lattice relaxation time T_1 according to the Kubo–Tomita equation [3]

$$\frac{1}{T_1}=A\left[\frac{\tau_c}{1-\omega^2\tau_c^2}+\frac{4\tau_c}{1+4\omega^2\tau_c^2}\right], \tag{3}$$

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